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EVALUATION OF CVD COATINGS DEVELOPED AT ORF II - TiB_2 ON DOUBLE-BULLET SHAPED SPECIMENS

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EVALUATION OF CHEMICAL VAPOUR DEPOSITION COATINGS DEVELOPED AT ORF II - TiB_2 ON DOUBLE-BULLET SHAPED SPECIMENS

by

A.W. Lui* and Y. Lafreniere**

ABSTRACT

Corrosion tests of a TiB_2 coating developed at the Ontario Research Foundation (ORF) revealed that a significant amount of iron (as high as 80.4 g/L in 24 h) was leached out from the metal substrate through the coating. The coating was applied to specimens by chemical vapour deposition (CVD) in 1% SO_2 - 99% N_2 at 800°C, the specimens were then immersed in 10% H_2SO_4 solution at 50°C. On the basis of previous results (2) and those obtained from the present study it can be concluded that the TiB_2 coating affords inadequate protection for metallic components under conditions used in high temperature coal conversion processes.

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LABORATOIRES DE RECHERCHE EN MÉTALLURGIE PHYSIQUE
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ÉVALUATION DU REVÊTEMENT PAR VAPEUR CHIMIQUE EXPLOITÉ À L'ORF
II - TiB_2 DES SPECIMENS SOUS FORME DE CYLINDRE À BOUTS RONDS

par

A.W. Lui* et Y. Lafreniere**

RÉSUMÉ

Des essais de corrosion d'une couche de TiB_2 mis au point à l'ORF (Ontario Research Foundation) ont révélé qu'une quantité considérable de fer (jusqu'à 80,4 g/L en 24 heures) avait filtré à travers la couche à partir du substrat métallique. L'application de la couche avait été effectuée au moyen du dépôt par vapeur chimique de 1% SO_2 - 99% N_2 à 800°C, ensuite on avait immergé les specimens dans une solution de 10% H_2SO_4 à 50°C. Par suite des résultats obtenus précédemment (2) et ceux produits par la présente étude, on doit conclure que, pour les pièces métalliques, la couche TiB_2 n'offre pas assez de protection contre les conditions rigoureuses présentées par les procédés de conversion du charbon à haute température.

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INTRODUCTION

The serviceability of metallic components in the operating environments of advanced fossil energy conversion and utilization processes has been identified as one of the more serious restraints to development. Refractory coatings to provide added protection to metal components against attack of service environments is one attractive way to address the problem. An example of one such coating is TiB_2 applied by CVD.

As a result of an unsolicited proposal, the Ontario Research Foundation was asked in 1981 to develop a CVD process for coating metal samples with TiB_2 (Contract No. 1SQ81-00070). The contract was joint funded by PMRL/CANMET, IMRI/NRC and DSS. A second contract in 1982 for further development of this coating (Contract No. OSQ82-00092) was funded by CANMET. In early work, TiB_2 coatings were deposited on coupons (30 mm x 25 mm x 0.76 mm) of carbon steel, and ferritic and austenitic stainless steels (1) and the performance of some coatings assessed at PMRL by exposure at 900°C in synthesized flue gas and ash deposit (2). Specimens failed these tests although they had earlier passed a 10% H_2SO_4 immersion test at ORF. It was suspected that failure occurred because of the poor quality of the deposit along the edges of the coupon. Thus, to improve coating adherence and quality, modifications were made to the specimen geometry and deposition variables (3). The improved specimen geometry consisted of wing cylinders 10 mm in diameter with hemispherical ends, the total length of the specimens being 20 mm. Subsequently, the protection performance of coatings was assessed by exposure to SO_2 at elevated temperatures and to H_2SO_4 solutions. It is these data which are discussed here.

EXPERIMENTAL

The apparatus for SO_2 corrosion testing, consisted of a tubular multi reactor heated by a horizontal furnace. The temperature of the furnace (800 ± 3°C) was controlled by a thermocouple connected to a thermo-controller monitored by a digital temperature indicator. In the H_2SO_4 solution test, the solution temperature was maintained at 50° ± 2°C by a constant temperature water bath with thermostatic control.

Cylindrical specimens of 1040 steel with hemispherical ends were coated with TiB_2 by CVD at ORF to a thickness of 75 μm. An intermediate layer of TiC or dull nickel was deposited on the metal substrate prior to the CVD process to improve the adherence of the coating (details may be found in Ref. 3). Some coated specimens were exposed to atmospheres of 1% SO_2 in nitrogen at 800°C for 24 to 48 h followed by cooling to room temperature in nitrogen, before they were placed in 25 mL of 10% H_2SO_4 at 50°C. Other as-received specimens were subjected directly to 25 m/L of 10% H_2SO_4 without exposure to SO_2. During the H_2SO_4 test, the thermocouple hole (drilled in the specimen for the CVD coating process) was kept above the liquid level. Same liquid level was maintained during the run by replenishing evaporation losses with distilled water. The solutions were then analysed by the atomic absorption technique for iron concentration as an indicator of coating performance.

RESULTS AND DISCUSSION

Results of preliminary tests of specimen A-4 (ORF No.) in 1% SO_2 for 144 h at 800°C and specimen B-1 with CaO applied to the coated surface in 1% SO_2 for 68 h at 800°C are shown in Fig. 1. Severe coating degradation suggested a shorter testing period or less severe testing conditions should be used.

In Fig. 2 (a and b), specimens D-2, D-8, D-15, D-19 and D-20 exposed to 1% SO_2 at 800°C for 24 h followed by 24 h of 10% H_2SO_4 exposure at 50°C are shown. Iron leached from the metal substrate through the TiB_2 coating ranged from 2.43 g/L for specimen D-8 to 80.40 g/L for specimen D-15 (under the same conditions the uncoated specimen B-4 gave an iron concentration of 84.2 g/L). In Fig. 3 (a and b), specimens D-3, D-5, D-11 and D-17 tested in 1% SO_2 for 48 h at 800°C followed by 8 h in 10% H_2SO_4 at 50°C are shown. The iron loss ranged from 0.21 g/L for specimen D-5 to 34.00 g/L for specimen D-11. In Fig. 4 (a and b), the as-received specimens D-38, D-40, D-41 and D-42 are shown after exposure to 10% H_2SO_4 solution at 50°C for 8 h. Iron loss ranged from 2.39 g/L for specimen D-38 to 10.90 g/L for specimen D-40. The wide range of iron concentrations detected by analysis suggested there was a significant difference in the quality of the coatings.

Although the specimen shape was chosen to eliminate edge effects during deposition and the rate of cooling during the CVD process was also modified to prevent spalling (3), most as-received specimens showed imperfections in the coatings, including "peeling off" and cracking. On the basis of these simple experiments it can be concluded that as deposited by the CVD process, TiB_2 coatings are not adequate to provide protection to metal components in high temperature coal conversion systems.

CONCLUSIONS

1. The testing of TiB_2 coatings in 1% SO_2 at 800°C followed by 10% H_2SO_4 at 50°C revealed that the iron leached out from the metal substrate through the coating could reach as high a concentration as 80.40 g/L in 24 h.

2. The iron leached from the metal substrate through the TiB_2 coatings in the as-received condition in a 10% H_2SO_4 solution ranged from 2.39 g/L to 10.90 g/L in 8 h.

3. On the basis of these simple tests, the coating is not considered suitable for use in protecting metal components in high temperature coal conversion processes.

ACKNOWLEDGMENT

The iron concentration analysis was done by the Chemical Laboratory of the Mineral Science Laboratories.

REFERENCES

1. Sze, W., Shimizu, H. and Gibbon, W.M., "Protective coatings for components of fossil energy conversion systems"; ORF Final Report (under DSS contract No. ISO81-00070); August 1982.

2. Lui, A.W. and McGoey, J., "Evaluation of CVD coatings developed at ORF for use in fossil energy conversion system; I-TiB_2 on carbon steel"; PMRL Report ERP/PMRL 82-17(TR); March 1982.

3. Shimizu, H. and Gibbon, W.M., "Chemical vapour deposited coatings for high temperature corrosion resistance"; ORF Final Report (under DSS contract No. OSQ82-00092); April 1983.

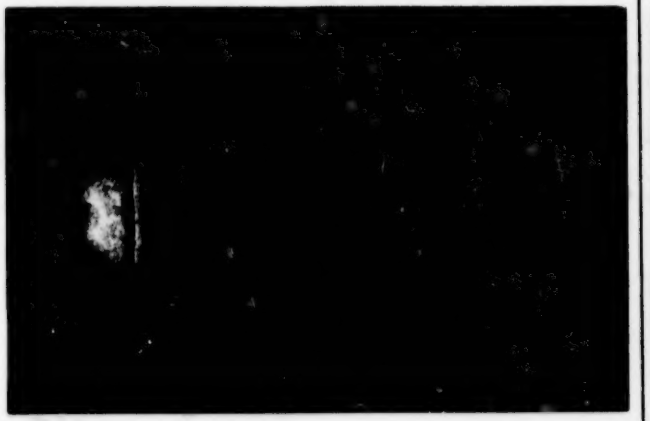
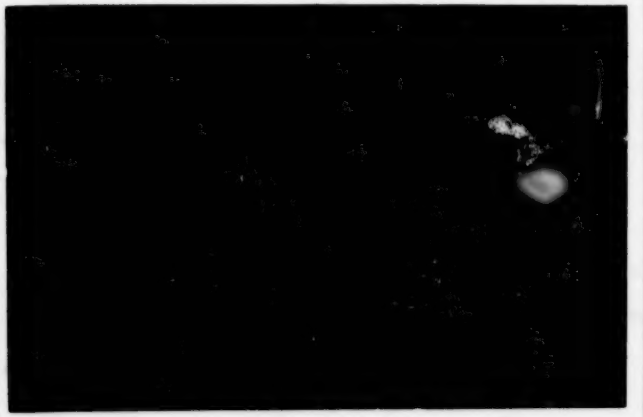
Specimen (ORF NO)	As Received	after SO_2 corrosion	Remarks
A-4			A-4 was exposed to 1% SO_2 for 144 h.
B-1			B-1 was coated with CaO slurry then exposed to 1% SO_2 for 68 h.

Fig. 1. Preliminary testing of TiB_2 coated specimens.

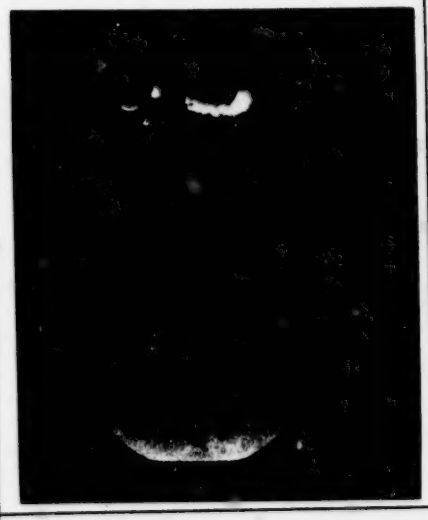
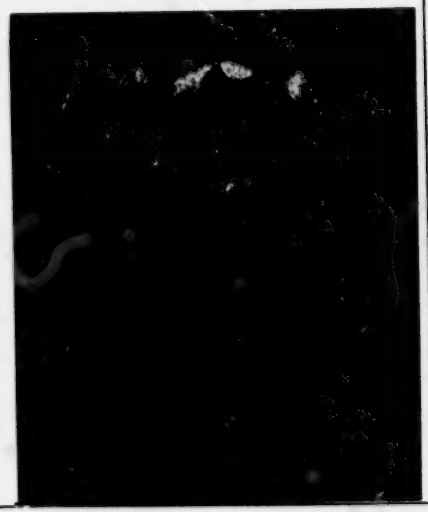
Specimen (ORF No)	As Received	after 24 h SO_2 corrosion	after 24 h H_2SO_4 leaching	[Fe] in H_2SO_4
D-2				14.4 g/L
D-8				2.43 g/L

Fig. 2. Corrosion of TiB_2 coating in 1% SO_2.

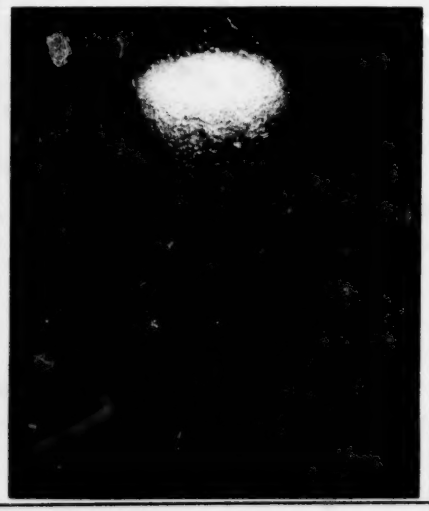
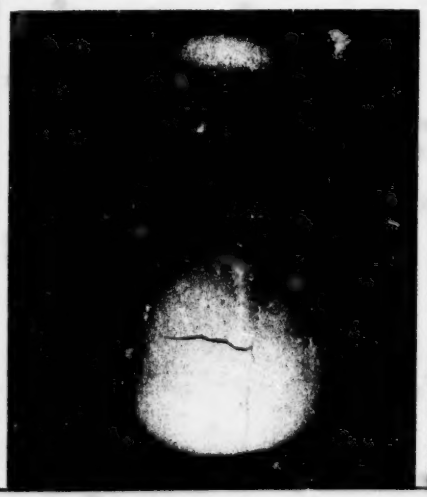
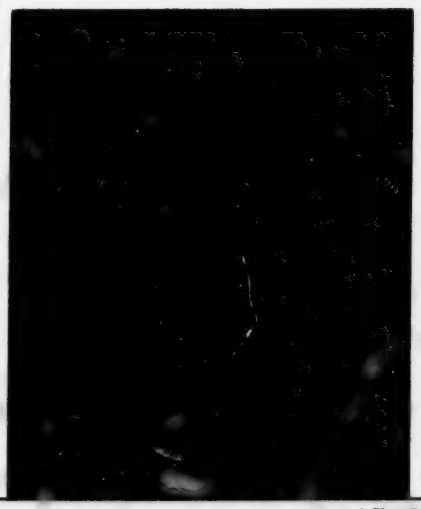
Specimen (ORF No)	As Received	after 24 h SO_2 Corrosion	after 24 h H_2SO_4 Leaching	[Fe] in H_2SO_4
D-15				80.4 g/L
D-19				57.6 g/L

Fig. 2(a) Corrosion of TiB_2 coating in 1% SO_2.

Specimen (ORF NO)	As Received	After 24 h SO_2 Corrosion	After 24 h H_2SO_4 Leaching	[Fe] in H_2SO_4
D-20				31.0 g/L
B-4	bare metal			84.2 g/L

Fig. 2(b). Corrosion of TiB_2 coatings in 1% SO_2.

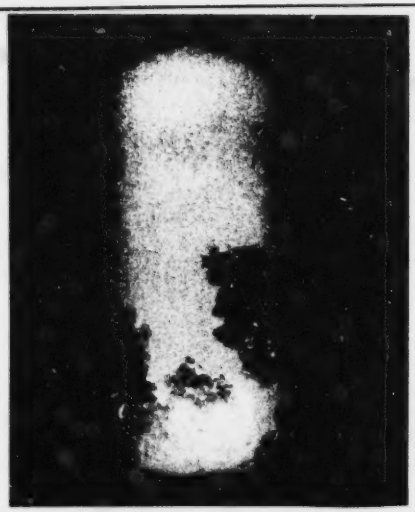
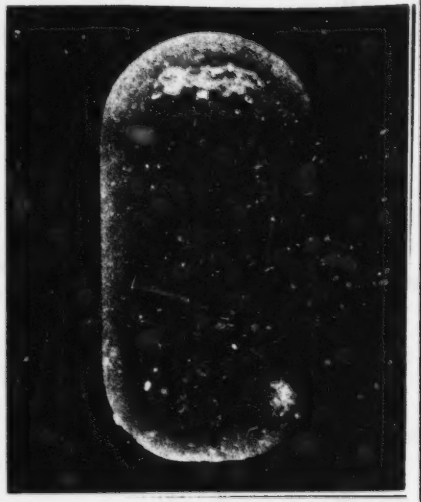
specimen (ORF NO)	As Received	after 48 h SO_2 Corrosion	after 8 h H_2SO_4 Leaching	[Fe] in H_2SO_4
D-3				9.58 g/L
D-5				0.21 g/L

Fig. 3(a) Corrosion of TiB_2 coating in SO_2.

Specimen (ORF NO.)	As Received	after 48 h SO_2 Corrosion	after 8 h H_2SO_4 Leaching	[Fe] in H_2SO_4
D-11				34.0 g/L
D-17				6.56 g/L

Fig. 3(b). Corrosion of TiB_2 coating in SO_2.

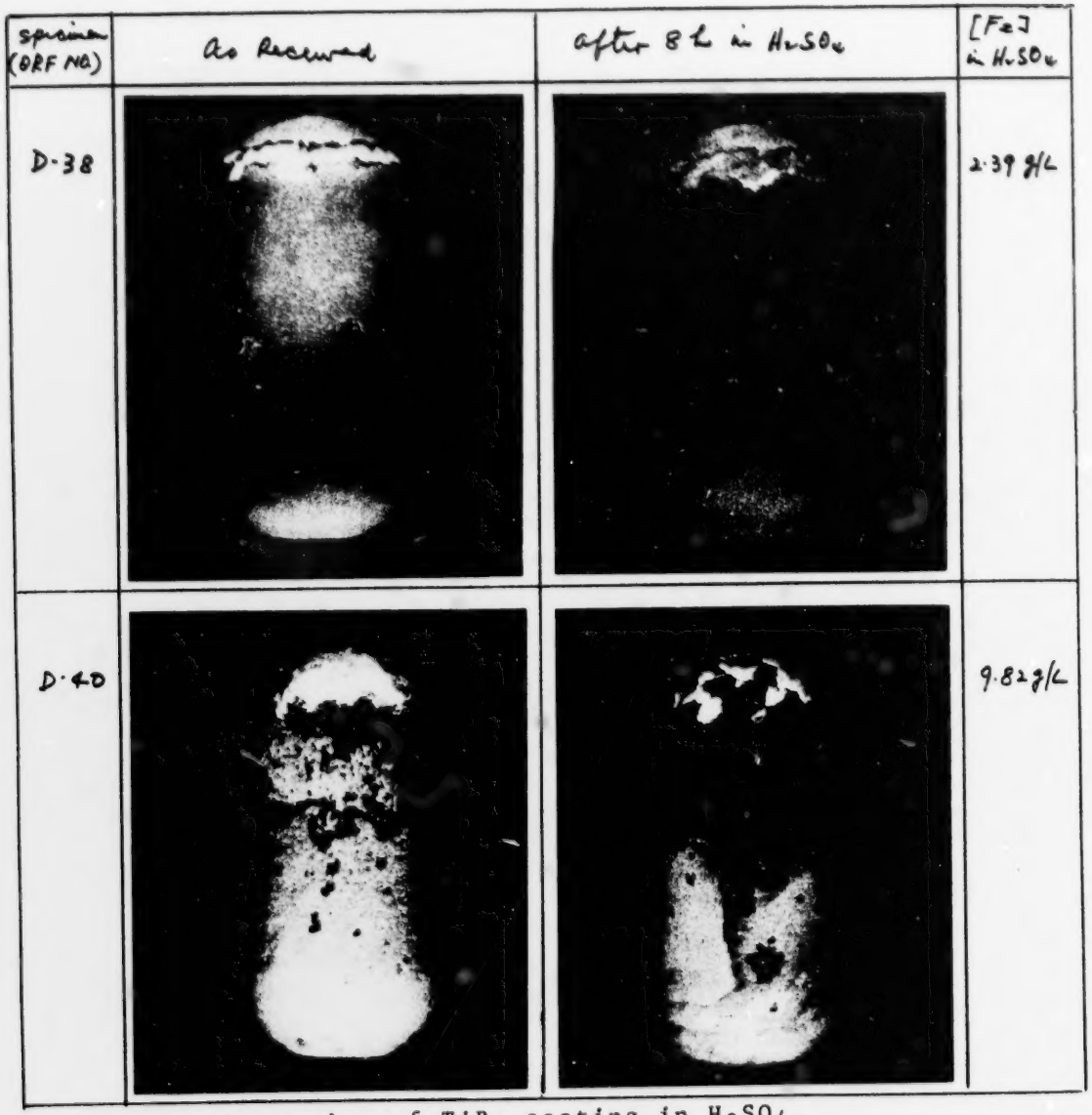


Fig. 4. Corrosion of TiB_2 coating in H_2SO_4.

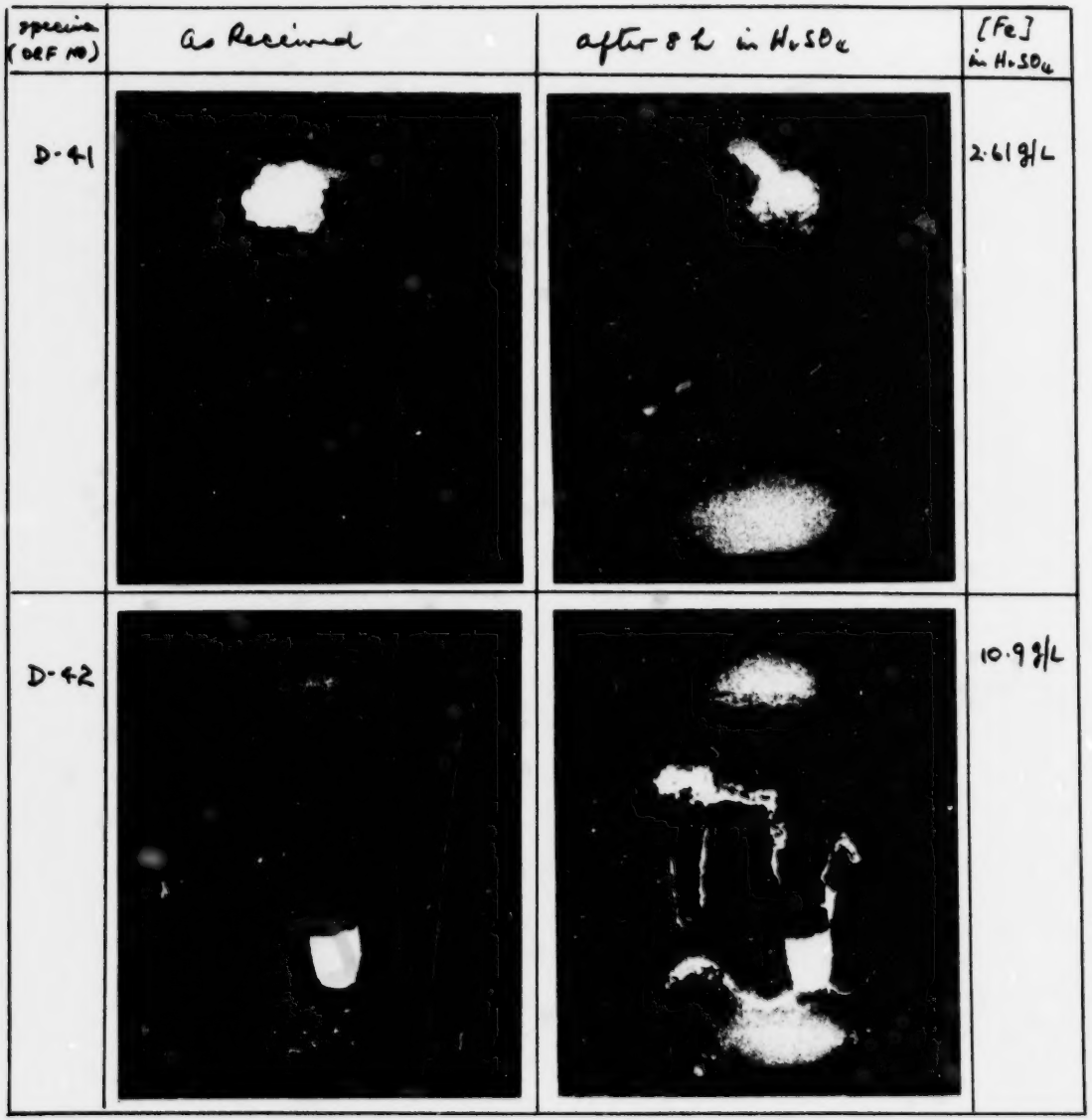


Fig. 4(a) Corrosion of TiB_2 coating in H_2SO_4.

List of Figures and Negative numbers

Figures	Negative	Figures	Negatives
1	9574	3(b)	9583
	9573		9561
	9575		9560
	9576		9584
2	9564		9562
	9565		9563
	9566	4	9548
	9568		9547
	9564		9546
	9569		9545
2(a)	9580		
	9578		
	9577		
	9560		
	9561		
	9562		
2(b)	9553		
	9554		
	9570		
	9571		
	9572		
3(a)	9555		
	9557		
	9556		
	9585		
	9559		
	9558		